Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 86 (2016) 171 – 180

Energy Procedia

The 8th Trondheim Conference on CO_2 Capture, Transport and Storage

Evaluating the activity and stability of CaO-based sorbents for post-combustion CO_2 capture in fixed-bed reactor experiments

Zinovia Skoufa[a]*, Andy Antzara[a], Eleni Heracleous[b,c], Angeliki A. Lemonidou[a,b]

[a]*Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece*
[b]*Chemical Process & Energy Resources Institute, CERTH, Thessaloniki 57001, Greece*
[c]*School of Science & Technology, International HellenicUniversity, Thessaloniki 57001, Greece*

Abstract

Carbonate Looping is a post-combustion CO_2 capture technology in which CO_2 is captured by a CaO-based sorbent. In this work, we report the development, preliminary evaluation and bench-scale testing of synthetic and natural sorbents. After preliminary screening, the most promising materials were studied in a fixed bed reactor under realistic flue gas feed composition. Zr and Al-doped synthetic CaO based sorbents exhibited very high sorption capacity and stability, due to their porous structure that is retained after 20 consecutive carbonation/calcination cycles. The natural sorbents presented inferior results, however their regeneration via hydration seems possible. The presence of steam in the flue gases seems to enhance sorption capacity and stability.

Peer-review under responsibility of the Programme Chair of the 8th Trondheim Conference on CO_2 Capture, Transport and Storage

Keywords: calcium looping; CO_2 capture; CaO-based sorbents; fixed-bed reactor tests; sorbent regeneration;

1. Introduction

Carbon dioxide (CO_2) is by far the most important of greenhouse gases, mainly due to its abundance [1,2]. Research aiming at mitigating CO_2 emissions particularly from power plants has received a lot of attention. Among several available processes for carbon dioxide capture, CO_2 capture with amines is a well-established technology that however suffers from serious problems of energetic/economic and environmental importance [3–5]. Therefore, alternative

* Corresponding author. Tel.: +30-2310-996077; fax: +30-2310-996184.
E-mail address: zskoufa@auth.gr ; zskoufa@gmail.com

Peer-review under responsibility of the Programme Chair of the 8th Trondheim Conference on CO_2 Capture, Transport and Storage
doi:10.1016/j.egypro.2016.01.018

processes for CO_2 separation are extensively investigated, including reactive CO_2 separation using dry, solid sorbents such as limestone, alkali zirconates/silicates and sodium carbonates [6]. The choice of suitable materials depends mainly on the type of the application that CO_2 capture is intended for. Considering CO_2 removal from flue gases originating from large stationary sources (e.g. power plants), sorbent properties such as heat tolerance, sorption capacity and stability, fast kinetics are very important for the economic viability of the process. Cost is also a major factor for such large scale applications.

In this context, calcium oxide is a very attractive material for carbon dioxide capture, mainly due to high theoretical CO_2 capture capacity of 0.786 g CO_2/g sorbent (17.8 mmol CO_2/g sorbent) and fast kinetics of the CO_2 capture and release reaction [7]. Carbonate Looping (CaL) is an ex-situ, post-combustion CO_2 capture technology based on the reversible reaction of calcium oxide with carbon dioxide to produce calcium carbonate. In a calcium looping cycle, the CaO-based sorbent is continuously transferred between two reactors: the carbonator, where the flue gases are stripped from CO_2 by the forward reaction of CO_2 uptake, and the calciner, where the formed $CaCO_3$ is decomposed to regenerated CaO producing at the same time a concentrated CO_2 stream ready to be sequestrated or used as raw material in downstream chemical processing units. The carbonation reaction is exothermic and the heat released can be integrated for the realization of the endothermic reverse reaction (calcination) for sorbent regeneration. The typical temperature window for CO_2 capture from a gas-fired flue gas stream ranges between 600ºC-650ºC in the carbonator and above 850ºC in the calciner [6,7].

Key for the large scale deployment of this process is sorbent development. In view of the carbonation reaction, CO_2 sorption process can be divided into two distinct steps: (i) an initial fast surface reaction controlled by the reaction kinetics and (ii) a slower reaction restricted by the diffusion of CO_2 in the $CaCO_3$ product [4]. An important aspect of the carbonation reaction is the difference in the molar volume of CaO and the product $CaCO_3$. Therefore, the formation of $CaCO_3$ results in the formation of a product layer of high molar volume which in turn leads to pore blockage [7]. Taking the above into consideration, it is obvious that the sorption capacity of a CaO-based material greatly depends on its morphological and structural characteristics, mainly its surface area and porosity. Moreover, taking into account that in practice such a process comprises several consecutive carbonation/calcination cycles, sorbent cyclic stability in multi-cycle operation is prerequisite for the successful industrial implementation of the calcium looping process. CaO derived from the decomposition of naturally occurring limestone, although cheap, has the major drawback of rapidly decreasing CO_2 capture capacity with a number of repeated carbonation and calcination cycles [8]. Several efforts to enhance physicochemical and sorption characteristics of calcium oxide have been employed: preparation of synthetic CaO, improvements in the synthesis methods and synthesis of CaO-based mixed oxides. These efforts include preparation of synthetic pure CaO sorbents via different Ca-precursors, different preparation methods as well as doping with a second metal and/or incorporation of inert materials and have indeed proved to be efficient, especially in terms of cyclic stability enhancement [9,10].

It is generally accepted that operating conditions, including for example reactor system employed, carbonation/calcination temperature and feed composition, affect to a significant extent the evaluation results on sorption capacity and stability [11]. Steam, which is anyway present in flue gases, is reported to enhance sorption capacity [12,13], whereas no positive effect was reported in other studies [14]. Steam has been also used for regeneration attempts of the sorbents, usually via the incorporation of a hydration step in the calcium looping cycle [15,16].

In this work, we report the development, preliminary evaluation and bench-scale testing of synthetic and natural mixed CaO-based sorbents for post-combustion CO_2 capture from industrial plants flue gases. The synthetic materials consist of CaO-based mixed oxides with Al, Zr, La and Mg, prepared via sol-gel auto-combustion synthesis using citric acid as a combustion agent. Concerning the natural CO_2 sorbents, we investigated the effect of different pre-treatments on the sorption capacity and stability of industrial hydrated lime. Mixing with inert minerals, such as kaolin, bauxite and magnesia, was attempted in an effort to reduce sintering and degradation under consecutive sorption/desorption cycles. The most promising materials were further studied at bench-scale in a fixed bed reactor, under a flow of CO_2, O_2, H_2O and N_2 simulating typical flue gases composition from a power plant. The possibility of hydration-induced regeneration and the effect of steam in flue gases are also investigated for selected materials.

2. Experimental

2.1. Sorbent synthesis

Four CaO-based powders promoted with Al, Zr, La and Mg were prepared by sol-gel auto-combustion synthesis using citric acid as combustion agent. The starting material was $Ca(NO_3)_2 \cdot 4H_2O$ (J.T.Baker) and the corresponding precursor for each promoter ($Al(NO_3)_3 \cdot 9H_2O$ (Carlo Erba), $La(NO_3)_3 \cdot 6H_2O$ (Merck), $Mg(NO_3)_2 \cdot 6H_2O$ (J.T.Baker) and $ZrO(NO_3)_2 \cdot xH_2O$ (Acros)). All sorbents were prepared with a constant 66wt% concentration of free CaO. The required amounts of calcium nitrate and the precursor of each promoter were dissolved in distilled water under continuous heating and stirring. Subsequently, the required amount of citric acid was added to the aqueous solution in order to maintain a constant nitrate salts/combustion agent molar ratio equal to 3. The new solutions were heated on a heating plate to promote water evaporation. After gelation occurred, the formed gel was transferred to a preheated furnace at 300°C, where after a few minutes the gel was combusted in a self-propagating combustion manner. The as synthesized powders were then calcined at 900°C for 1.5 hour under air flow. The sorbents are denoted as Ca-X, where X refers to the promoter (Zr, La, Mg or Al).

Hydrated lime, $Ca(OH)_2$, provided by CaO Hellas was investigated as CaO source for natural CO_2 sorbents. Three different pre-treatment protocols were tested for the activation of raw $Ca(OH)_2$: Protocol 1: the raw material was calcined at 900°C for 1.5 hour under air flow ($Ca(OH)_2$-C900), Protocol 2: the calcined sample was then hydrated with water at 70°C for 4 hours to increase the surface area and as a result the sorption capacity, and was finally recalcined at 600°C for 3 hours in order to decompose the formed $Ca(OH)_2$ during hydration ($Ca(OH)_2$-W-C600) and Protocol 3: same as protocol 2, excluding final calcination step which was conducted at 900oC ($Ca(OH)_2$-W-C900). Three natural heat resistant binders were used as means to increase cyclic stability, namely kaolin, bauxite and magnesia. Kaolin is a mineral composed mainly of Al2O3 and SiO with a general formula of $Al \cdot 2SiO_2 \cdot 2H_2O$, bauxite is composed mainly of Al_2O_3 and Fe_2O_3 while the magnesia was mainly MgO with less than 3% impurities. Three methods were investigated for the incorporation of the binders: Protocol 4: $Ca(OH)_2$-W-C600 sample obtained from protocol 2 was mixed with Kaolin ($Ca(OH)_2$-KAOL), Bauxite ($Ca(OH)_2$-Baux) or MgO ($Ca(OH)_2$-MgO) in distilled water at 70°C under continuous stirring for 4 hours. The materials were filtered, dried overnight at 120°C and calcined at 900°C for 1.5 hr under air flow; Protocol 5: raw $Ca(OH)_2$ instead of $Ca(OH)_2$-W-C600 was used as the CaO-precursor, and MgO ($Ca(OH)_2$-MgO-RW) or Bauxite (Ca(OH)2-Baux-RW) was added following the same procedure as in protocol 4; Protocol 6: raw $Ca(OH)_2$ and MgO were grinded in a mortar for 20min and the resulting mechanical mixture was calcined at 900°C for 1.5 hr under air flow.

Mixed natural sorbents were all prepared with a constant 66wt% concentration of free CaO.

2.2. Physicochemical characterization

Surface areas of the samples were determined by N_2 adsorption at 77 K, using the multipoint BET analysis method, with an Autosorb-1 Quantachrome flow apparatus. Prior to the measurements, the samples were dehydrated in vacuum at 250 °C overnight.

X-Ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, with Cu-Kα radiation.

The morphology of the synthesized materials was examined by scanning electron microscopy (SEM) on a JEOL 6300 microscope, coupled with energy-dispersive X-ray analysis (EDX; Oxford Link ISIS-2000) for local elemental composition determination.

2.3. Preliminary evaluation in TGA

An SDT Q600 (TA Instrument) thermal gravimetric analysis (TGA) instrument was used for the preliminary evaluation of all sorbent in 100 consecutive carbonation/calcination experiments. SDT Q600 works in conjunction with a controller and associated software to make up a thermal analysis system. A small quantity of the material (5–10 mg), placed in an aluminum sample cup, was pretreated at 850 °C, in the presence of 100 cm^3/min pure N_2, for 10 min to remove possible humidity and CO_2 absorbed. The CO_2 capacity of the sorbents was tested under 15% CO_2 flow in N_2 for

30 minutes at 650ºC while desorption took place under 100% N_2 flow for 5 minutes at 850ºC. Results are presented in terms of sorption capacity of the materials (mol CO_2/kg of sorbent) and CaO conversion

2.4. Fixed-bed reactor experiments

The most promising synthetic and natural sorbents according to preliminary evaluation in TGA were tested in a bench scale flow unit for 20 consecutive CO_2 sorption/desoption cycles. A fixed bed quartz reactor with 18 mm external diameter of the reactor tube in the reaction zone and equipped with coaxial thermocouple for temperature monitoring was used for testing. The reactor was heated electrically by a tubular furnace, with three independently controlled temperature zones. Carbonation was conducted at 650ºC under a 10% CO_2/ 20% H_2O/ 3.2% O_2/ N_2 feed. Calcination was conducted at 800ºC in a 30%H_2O/N_2 flow. The CO_2 concentration in the reactor exit was monitored online by a CO_2 analyzer (Horiba, VIA 510).

3. Results and discussion

3.1. Physicochemical characterization

According to XRD analysis (not shown here for brevity), the main crystal phase formed in all synthetic CaO-based sorbents is CaO, accompanied by minor peaks of low intensity corresponding to $Ca(OH)_2$ in Ca-Mg, Ca-Al and Ca-Zr samples. Formation of mixed $Ca_3Al_2O_6$ and $CaZrO_3$ was observed in Ca-Al and Ca-Zr sorbents, respectively. On the contrary no mixed phase was formed between CaO and Mg or La, where the precursor nitrate salts decomposed to MgO and La_2O_3 respectively [17]. Concerning the textural properties of the synthetic sorbents, summarized in Table 1, it can be observed that the nature of the dopant affects the surface area of the final material. Surface areas ranging from 28 m^2/g for Mg-doped CaO to 9 m^2/g for La-doped CaO were recorded.

Table 1. BET surface area and pore volume of the synthetic and natural CaO-based sorbents.

Sorbent	Surface area (m^2/g)	Pore volume (cm^3/g)
Ca-Mg	28.4	0.112
Ca-La	8.8	0.138
Ca-Zr	20.5	0.051
Ca-Al	12.5	0.062
$Ca(OH)_2$-C900	5.04	0.041
$Ca(OH)_2$-W-C600	17.2	0.181
$Ca(OH)_2$-W-C900	16.8	0.149
$Ca(OH)_2$-KAOL	3.2	0.023
$Ca(OH)_2$-Baux	5.2	0.0198
$Ca(OH)_2$-MgO	23.3	0.427
$Ca(OH)_2$-Baux-RW	5.29	0.029
$Ca(OH)_2$-MgO-RW	25.49	0.199
$Ca(OH)_2$-MgO-GM	18.7	0.13

The as delivered industrial material ($Ca(OH)_2$) is composed of almost pure calcium hydroxide, with only a small reflection corresponding to calcium carbonate. After thermal pre-treatment at 900ºC ($Ca(OH)_2$-C900), $Ca(OH)_2$ was almost completely decomposed to CaO with minor $Ca(OH)_2$ reflections. When the calcined sample was subjected to water treatment and calcined, only reflections at the angular positions of $Ca(OH)_2$ appear, despite the high temperature used in calcination either at 600ºC or at 900ºC, that was expected to favour hydroxide decomposition to CaO. The addition of kaolin leads to the formation of a mixed phase $Ca_3Al_2Si_2$, together with pure Al_2O_3 and SiO_2. Regardless of the preparation method, in the case of the use of bauxite or MgO as binders, the XRD patterns revealed the existence of

CaO and MgO or Al_2O_3 crystalline phases, together with low intensity peaks corresponding to $Ca(OH)_2$ in the case of $Ca(OH)_2$-Baux and $Ca(OH)_2$-Baux-RW samples, without any formation of mixed components. The surface area and pore volume of all natural CaO-based sorbents is presented in Table 1. Hydration of the calcined sample leads to an increase in surface area and porosity compared to $Ca(OH)_2$-C900 sample [15]. Concerning the mixed materials, the nature of the binder seems to affect the textural properties of the final sorbent. The introduction of kaolin or bauxite in industrial hydrated lime decreases the surface area. On the contrary, the use of MgO greatly increases the surface area to ~25m^2/g which can be partly attributed to the high surface area of pure MgO (70m^2/g). Overall, it can be concluded that basic physicochemical characterization of the natural sorbents revealed no important effect of the preparation method, whereas doping with MgO seems to greatly affect both surface area and porosity.

3.2. Preliminary evaluation in TGA

The performance of synthetic and natural sorbents the four promoted synthetic CaO sorbents in the TGA carbonation-calcination tests is summarized in Table 2. Although a wide range of surface areas was observed, all the promoted sorbents (with the exception of Ca-La) achieved very high CaO conversions (>80%) that could be attributed mainly to the nature of the dopants and the formed structure of the final materials during combustion synthesis [17]. All of the doped sorbents, except Ca-La, exhibit a very stable performance during the first 70 cycles, unlike the pure CaO prepared with citric acid which deactivates very fast in the first 20 cycles. Doping with Zr leads to the development of the most stable sorbent, followed closely by Al, while Ca-Al sorbent exhibits the highest initial sorption capacity.

Concerning natural sorbents consisting of pure CaO, water treatment of the industrial hydrated lime greatly increases the initial CO_2 sorption capacity compared to the sample directly calcined at 900ºC, but unfortunately in expense of stability. Sample $Ca(OH)_2$-C900 presents the highest sorption capacity and stability. The use of kaolin, bauxite and MgO binders leads to a decrease initial CO_2 sorption capacity due to the lower content of CaO in the materials, with the exception of $Ca(OH)_2$-MgO-RW and $Ca(OH)_2$-MgO-GM samples. Nevertheless, CaO conversion increases for all doped sorbents, indicating the beneficial effect of binders that seem to increase the accessibility of active calcium oxide surface. Overall, the most promising results were recorded for samples $Ca(OH)_2$-C900 and $Ca(OH)_2$-MgO-GM, that were prepared via a solvent-free method. These two sorbents, together with Ca-Al and Ca-Zr synthetic materials were chosen for further testing in a fixed bed reactor. It is obvious that the synthetic CaO-based sorbents exhibited almost twice the initial sorption capacity of the natural sorbent and a very stable performance with much lower deactivation after the same number of sorption/desorption cycles. However, the use of natural sorbents presents important economic and environmental advantages, since they are based on naturally occurring minerals.

Table 2. Preliminary evaluation results obtained from TGA (carbonation: 650ºC, 15%CO_2/N_2, 30 min; calcination: 850ºC, 100%N_2, 5min

	Initial capacity (mol CO_2/kg sorbent)	Initial CaO conversion (%)	Deactivation after 100 cycles (%)
Ca-Mg	10.37	88.0	29.7
Ca-La	9.05	76.8	37.7 (70 cycles)
Ca-Zr	10.63	90.2	13.7
Ca-Al	11.64	98.8	20.7
$Ca(OH)_2$-C900	5.22	29.2	36.9
$Ca(OH)_2$-W-C600	11.32	63.4	69.6 (50 cycles)
$Ca(OH)_2$-W-C900	8.26	46.2	47.5 (30 cycles)
$Ca(OH)_2$-KAOL	4.84	41.1	27.5 (50 cycles)
$Ca(OH)_2$-Baux	4.00	33.9	36.1
$Ca(OH)_2$-MgO	5.64	47.9	46.1
$Ca(OH)_2$-Baux-RW	4.26	36.1	32.3
$Ca(OH)_2$-MgO-RW	6.02	51.1	52.0
$Ca(OH)_2$-MgO-GM	4.54	38.5	31.1

3.3. Bench scale testing in a fixed-bed reactor

After initial sorbent screening in TGA, the most promising synthetic and natural sorbents were tested in a fixed bed reactor, under realistic feed conditions. Fig. 1 presents the results for Ca-Al and Ca-Zr testing in 20 consecutive carbonation/calcination experiments. It should be noted that the sorption capacity refers to the amount of CO_2 captured in the pre-breakthrough period, i.e in the carbonation stage controlled by surface reaction as will be discussed later on. Both synthetic sorbents present high sorption capacity and satisfactory stability. Given the differences between experimental set-ups, the sorption capacity recorded in these experiments is similar to the results obtained in TGA, which refer to the overall sorption capacity (not just in the pre-breakthrough period). Al-doped CaO based sorbent presents only 12.5% deactivation after 20 cycles, compared to 23% deactivation for Ca-Zr.

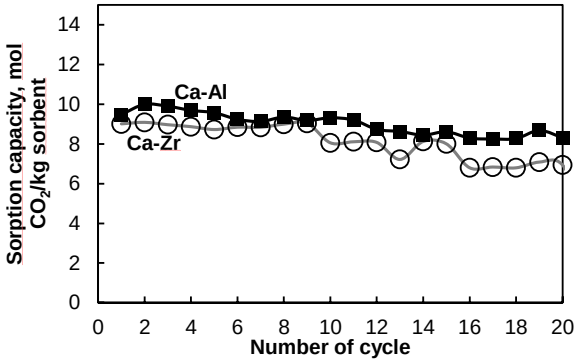

Fig. 1. Sorption capacity versus number of cycle for Ca-Zr (GHSV=318h^{-1}) and Ca-Al (GHSV=311h^{-1}) synthetic sorbents in fixed bed experiments (carbonation: 650ºC, 10% CO_2/ 20% H_2O/ 3.2% O_2/ N_2; calcination: 800ºC, 30%H_2O/N_2)

Carbonation profiles for the 1st and 20th cycle for Ca-Zr sorbent are presented in Fig. 2a, where CO_2 concentration at the reactor outlet is plotted versus time. According to the carbonation profiles, CO_2 capture proceeds via two distinctive stages. In the first stage, also known as the pre-breakthrough period, the rate determining step of carbonation is the surface reaction between CO_2 and CaO. During this period, the CO_2 concentration is maintained at very low levels (< 2%vol.), indicating a constantly high CO_2 capture rate. In the experimental conditions used, both synthetic sorbents approach thermodynamic equilibrium CO_2 conversion per pass. In the first cycle the duration of pre-breakthrough period for Ca-Zr sample is ~127 min (Fig. 2a). At that time ~80% CaO conversion is achieved, corresponding to a sorption capacity of 9.02 mol CO_2 /kg sorbent. As the formation of $CaCO_3$ proceeds, the overall CO_2 capture process is governed by diffusion of CO_2 through the $CaCO_3$ layer. This step is generally slower, and as shown in Fig. 2a, it is characterized by a fast increase of CO_2 concentration in reactor outlet. As already discussed, in a possible industrial implementation of the CaL concept, the sorbent would exit the carbonator before gradual diffusion becomes rate-controlling.

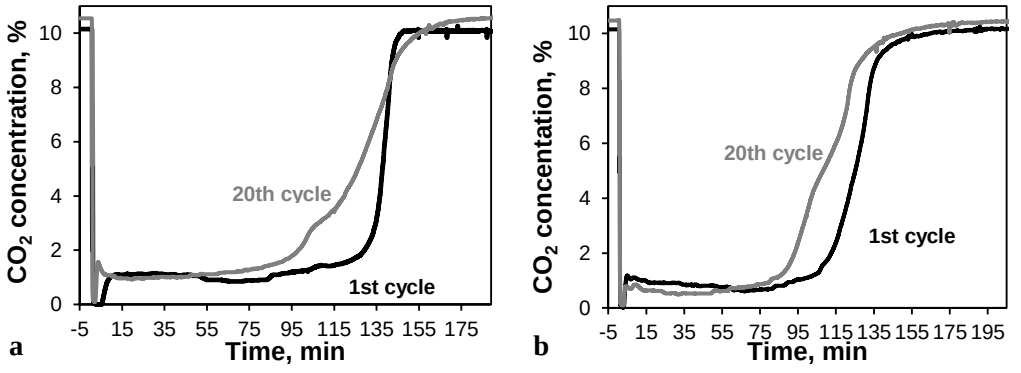

Fig. 2. CO_2 concentration at reactor outlet during the 1st (black line) and 20th (grey line) cycle of carbonation for (a) Ca-Zr and (b) Ca-Al samples (carbonation: 650ºC, 10% CO_2/ 20% H_2O/ 3.2% O_2/ N_2; calcination: 800ºC, 30%H_2O/N_2)

As shown in Fig. 2a for Zr-doped CaO-based sorbent, after 19 cycles the duration of the kinetically controlled period has decreased to 100 min in the 20th cycle, leading to sorbent deactivation by 23%. Characterization of the spent sorbent evidenced a 50% reduction in surface area (surface area of used sample: 11.1m^2/g). Moreover, characterization of the fresh and used samples with SEM revealed significant agglomeration of the material after 20 cycles. As shown in Fig. 3a (i), the fresh material is composed of small particles in the range of 10μm, whereas in the used sample agglomeration led to the formation of larger particles, some of which are as large as 500μm (Fig. 3a (iii)). Nevertheless, it seems that the porous structure of the sorbent is retained to a significant extent, in line with the moderate degree of deactivation that was recorded for Ca-Zr sorbent. Formation of $CaZrO_3$ mixed phase seems to be the key for the avoidance of extended sintering phenomena, as previously reported [18], due to its high Tamman temperature [19]. Characterization results of the used and fresh samples may constitute the basis for enlightening the deactivation mechanism of the sorbent. Due to surface area reduction, the carbonation reaction more quickly falls into diffusion-controlled regime. Nevertheless, total sorption capacity, calculated as the total amount of CO_2 that was captured throughout carbonation and not just in the pre-breakthrough period, is the same as in the first cycle. This result indicated that sorbent did not suffer any loss of intrinsic activity. The stable porous structure enables CO_2 diffusion to the bulk of Ca-Zr particles, even if this step is completed in a longer time after 20 cycles, as evidence by comparing the diffusion-controlled period in the 1st and 20th cycle (Fig. 2a).

Ca-Al synthetic sorbent presented high sorption capacity, equal to 9.49 mol $CO_2/kg_{sorbent}$ in the kinetically controlled stage which lasted for 110min, as shown in Fig. 2b. Compared to Ca-Zr sample, Ca-Al presented slightly higher CO_2 uptake rate, leading to higher sorption capacity despite the smaller pre-breakthrough period. In the 20th cycle, the surface reaction controlled step is reduced to 90 min. As discussed for the Zr doped sample, the deactivation of Ca-Al sorbent is attributed to a decrease in surface activity. The total active sites of the sorbent material do not decrease judging from the fact that the same total amount of CO_2 was captured in cycles 1 and 20. Characterization of the used sample showed a small decrease in surface area (from 12.5m^2/g to 9.3m^2/g) in line with a small deactivation rate of 12.5% after 20 carbonation/calcination cycles. The porous structure of the material seems to remain almost intact, despite the formation of small agglomerates, as shown in SEM micrographs (Fig. 3b).

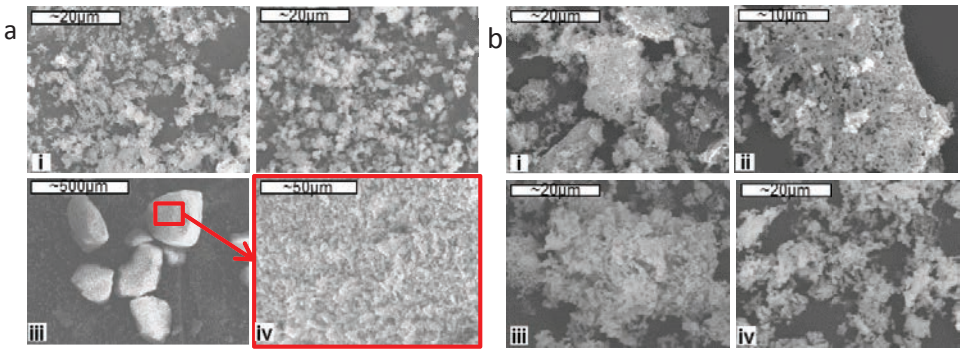

Fig. 3. (a) SEM micrographs of Ca-Zr sample: (i) fresh; (ii)-(iv) used after 20 cycles in fixed bed; (b) SEM micrographs of Ca-Al sample: (i), (ii) fresh; (iii), (iv) used after 20 cycles in fixed bed

As expected, $Ca(OH)_2$-C900 and $Ca(OH)_2$-MgO-GM natural sorbents presented significantly lower sorption capacity compared to synthetic sorbents, and intense deactivation in the first 5 cycles, as shown in Fig. 4 and Fig. 5 respectively. The carbonation profiles for both natural sorbents in the 1st cycle are shown in Fig. 6. Unlike synthetic sorbents, it can be observed that for the natural sorbents, the breakthrough period lasts longer than the pre-breakthrough period. In other words, the amount of CO_2 that is captured in the diffusion controlled regime is greater than in the kinetics-controlled regime, indicating different morphology between natural and synthetic sorbents. Indeed, pore size distribution evidenced the occurrence of smaller pores (mesopores) for natural sorbents compared to synthetic samples that mainly present macroporosity. Consequently, in natural sorbents the easily accessible surface sites are presumably less compared to synthetic sorbents. Moreover, unlike synthetic sorbents, for which the same activity results were obtained both in TGA and bench scale testing, both natural sorbents presented higher activity in the fixed bed reactor experiments compared to the preliminary results in TGA, in terms of total sorption capacity. This increase of total sorption capacity results from

both surface reaction- and diffusion controlled steps; however the pre-breakthrough period contributes the most to the observed total capture activity of the solids. In the TGA setup, the 15% CO_2/N_2 feed is inserted in the oven in a "flow over" mode as opposed to "flow-through" conditions in the fixed bed reactor. Moreover, in bench scale testing the presence of steam might affect the carbonation reaction, as previously suggested [12,13]. According the results reported in the present study, it can be deduced that the presence of steam enhances both steps of the carbonation reaction. Overall, based on the above, enhanced CO_2 diffusion to less easily accessible surface sites is probably the reason for the higher CO_2 capture efficiency recorded in the bench-scale experiments for natural sorbents.

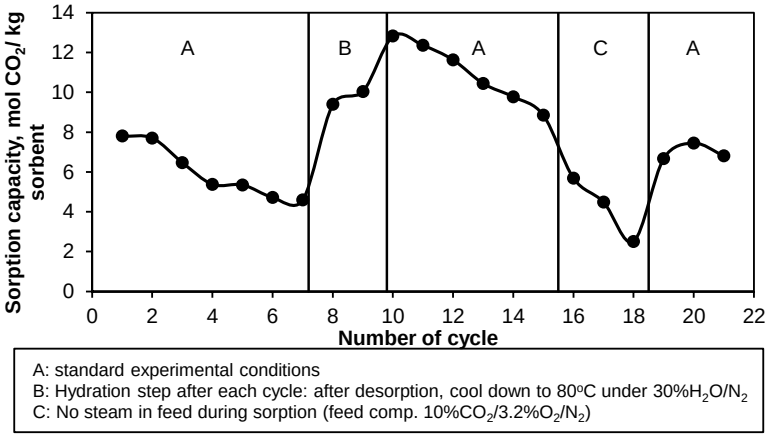

Fig. 4. Sorption capacity versus number of cycle for $Ca(OH)_2$-C900 (GHSV=286.5h^{-1}) natural sorbent in fixed bed experiments

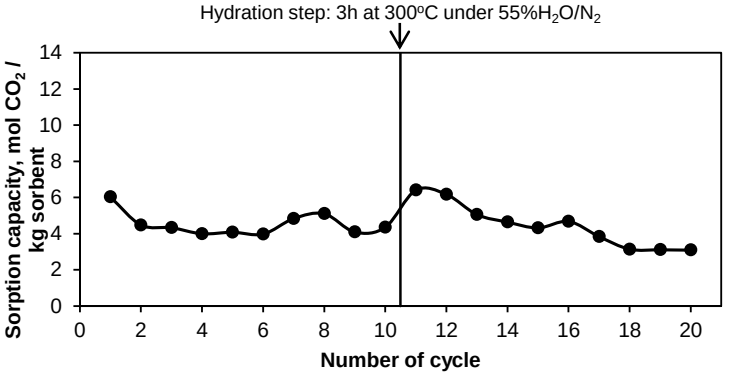

Fig. 5. Sorption capacity versus number of cycle for $Ca(OH)_2$-MgO (GHSV=427h^{-1}) natural sorbent in fixed bed experiments (carbonation: 650ºC, 10% CO_2/ 20% H_2O/ 3.2% O_2/ N_2; calcination: 800ºC, 30%H_2O/N_2)

Since the natural sorbents were significantly deactivated during the first 5 cycles, two different approaches were studied in an attempt to investigate the possibility of sorbent regeneration. Concerning $Ca(OH)_2$-C900 sorbent, after the 7^{th}, 8^{th} and 9^{th} cycle, the sample was cooled down from 800ºC (desorption temperature) to 80ºC, under a 30% H_2O/N_2 flow. According to the thermodynamic equilibrium curve for CaO hydration, calcium oxide is hydrated to calcium hydroxide at temperatures lower than 400ºC. The reaction is accompanied by an increase in specific volume, from 16.9 cm^3/mol for CaO 33.1cm^3/mol for $Ca(OH)_2$, ultimately resulting to an increase in surface area and porosity [15]. As shown in Fig. 4, the hydration procedure led not only to containment of sorbent deactivation, but also to a significant increase (~180%) in sorption capacity from cycle 7^{th} to 10^{th}. It should be noted here, that in case of process scale-up the addition of such a regeneration procedure would not be economically efficient, in terms of energy needs for cooling down and re-heating the regenerated sorbent. Cycles 10 to 15 were conducted without a hydration step, and as shown in Fig. 4, the sample was again deactivated following roughly the same trend as in the first six cycles. In order to investigate the

effect of steam presence in the flue gases, cycles 16, 17 and 18 were performed in the absence of steam in the feed, leading to a sharp decrease of the sorption capacity from 8.85 mol CO_2/kg in cycle 15 to 2.51 mol CO_2/kg in cycle 18. Overall, the above results indicate that the presence of steam in the feed increases CO_2 capture efficiency and promotes sorbent stability, most probably by facilitating CO_2 diffusion.

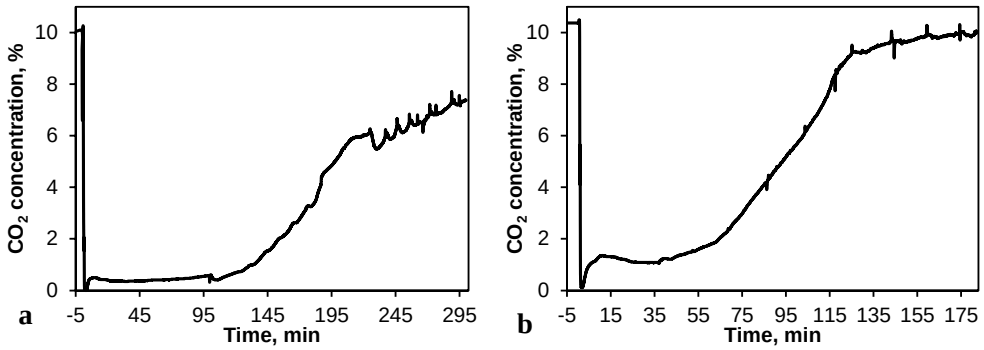

Fig. 6. Carbonation profiles for the 1st cycle for a) $Ca(OH)_2$-C900 (GHSV=286.5h^{-1}) and b) $Ca(OH)_2$-MgO-GM (GHSV=427h^{-1}) natural sorbents (650ºC, 10% CO_2/ 20% H_2O/ 3.2% O_2/ N_2)

As shown in Fig. 5, $Ca(OH)_2$-MgO-GM sorbent presents an initial sorption capacity of 6.03molCO_2/kg, and is deactivated by ~33% within the first 5 cycles. The second approach to regenerate the sorbents was then investigated for $Ca(OH)_2$-MgO-GM sorbent. After calcination at 800ºC, the sample was cooled down to 300ºC and left to react towards $Ca(OH)_2$ under a 55% H_2O/N_2 flow for 3h. This hydration process resulted in an increase in sorption capacity, as shown in Fig. 5. For the next cycles up until cycle 20 the carbonation/calcination procedure was repeated without any intermediate regeneration step and the sorbent continued to deactivate; an overall ~49% deactivation was finally recorded.

Table 3 summarizes the bench-scale results for CO_2 capture. It is obvious that the synthetic sorbents prepared by sol-gel auto-combustion synthesis presented superior capture activity and stability compared to the natural sorbents derived from industrial hydrated lime. In view of the important conclusions derived from the comparison of TGA and fixed bed reactor testing and characterization of spent solids, it can be deduced that the superiority of synthetic sorbents lies in their porous structure. On one hand, this porous structure enhances CO_2 capture by maximizing the available CaO surface. On the other hand, the addition of Zr and Al leads to the formation of thermally stable $CaZro_2$ and $Ca_3Al_2O_6$ mixed phases that provide stability. The final choice on whether synthetic or natural sorbents should be used in a potential scale up will be determined by techno economic factors, taking into account the cost of sorbent development versus the need for sorbent make-up due to deactivation.

Table 3. Summary of CO_2 capture results (pre-breakthrough time) obtained in the fixed bed reactor for the four selected sorbents

	Initial capacity (mol CO_2/kg sorbent)	Initial CaO conversion (%)	Deactivation after 100 cycles (%)
Ca-Zr	9.02	76.6	23
Ca-Al	9.49	80.6	12.5
$Ca(OH)_2$-C900	7.80	43.7	13*
$Ca(OH)_2$-MgO-GM	6.03	51.2	48.7*

*after (several) hydration steps, see text for details

4. Conclusions

CO_2 capture from flue gases via carbonation calcination cycles over CaO-based sorbents is a promising technology. In the present study, several synthetic and natural sorbents were developed and preliminary evaluated in TGA. Synthetic sorbents prepared by sol-gel auto-combustion technique exhibited high sorption capacity and stability.

Natural sorbents derived from industrial hydrated lime presented promising results; the preparation procedure seems not to significantly affect activity and stability. The most promising synthetic, Ca-Zr and Ca-Al, and natural, pure CaO derived from $Ca(OH)_2$ direct calcination and MgO-doped $Ca(OH)_2$, were tested in a fixed bed reactor under realistic flue gas feed composition. Zr and Al-doped CaO based sorbents exhibited very high sorption capacity and stability over 20 consecutive carbonation/calcination cycles, owing to the porous structure obtained by the auto-combustion technique and retained due to the presence of thermally stable Ca-Zr and Ca-Al mixed phases. The natural sorbents presented inferior results, however their regeneration via hydration seems possible, although most likely not economically viable. The presence of steam in the flue gases seems to enhance sorption capacity and stability. Ca-Al synthetic sorbent exhibited the most promising performance and shows great potential for process scale up.

Acknowledgements

We acknowledge the financial support from European Union-European Regional Development Fund and Ministry of Development, ESPA 2007–2013/EPAN II programme, Action Synergasia11'.

References

[1] Blockstein DE, Shockley MA. Energy for a Sustainable and Secure Future: A report of the Sixth National Conference in Science, Policy, and the Environment. Washington, DC; 2006.
[2] Fan L-S. Chemical Looping Systems for Fossil Energy Conversions. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2010.
[3] Mandal BP, Bandyopadhyay SS. Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanol and monoethanolamine. Chem Eng Sci 2006;61:5440–7.
[4] Wang J, Huang L, Yang R, Zhang Z, Wu J, Gao Y, et al. Recent advances in solid sorbents for CO_2 capture and new development trends. Energy Environ Sci 2014;7:3478–518.
[5] Blamey J, Anthony EJ, Wang J, Fennell PS. The calcium looping cycle for large-scale CO_2 capture. Prog Energy Combust Sci2010;36:260–79.
[6] Park A-HA, Gupta P, Li F, Sridhar D, Fan L-S. Novel applications of chemical looping technologies. In: Fan L-S, editor. Chemical Looping Systems for Fossil Energy Conversions. New Jersey, USA: AIChE, Wiley; 2010. p. 363.
[7] Broda M, Pacciani R, Muller CR. CO_2 Capture via Cyclic Calcination and Carbonation Reactions. In: Lu A-H, Dai S, editors. Porous Materials for Carbon Dioxide Capture Berlin Heidelberg: Springer; 2014. p. 181.
[8] Grasa GS, Abanades JC. CO2 capture capacity of CaO in long series of carbonation/calcination cycles. Ind Eng Chem Res 2006;45:8846–51.
[9] Martavaltzi CS, Lemonidou AA. Development of new CaO based sorbent materials for CO_2 removal at high temperature. Microporous Mesoporous Mater 2008;110:119–27.
[10] Angeli SD, Martavaltzi CS, Lemonidou AA. Development of a novel-synthesized Ca-based CO_2 sorbent for multicycle operation: Parametric study of sorption. Fuel 2014;127:62–9.
[11] Alonso M, Criado YA, Abanades JC, Grasa G. Undesired effects in the determination of CO_2 carrying capacities of CaO during TG testing. Fuel 2014;127:52–61.
[12] Kavosh M, Patchigolla K, Anthony EJ, Oakey JE. Carbonation performance of lime for cyclic CO_2 capture following limestone calcination in steam/CO_2 atmosphere. Appl Energy 2014;131:499–507.
[13] Manovic V, Anthony EJ. Carbonation of CaO-Based Sorbents Enhanced by Steam Addition. Ind Eng Chem Res 2010;49:9105–10.
[14] Sun P, Grace JR, Lim CJ, Anthony EJ. Investigation of Attempts to Improve Cyclic CO_2 Capture by Sorbent Hydration and Modification. Ind Eng Chem Res 2008;47:2024–32.
[15] Li Z, Liu Y, Cai N. Understanding the enhancement effect of high-temperature steam on the carbonation reaction of CaO with CO_2. Fuel 2014;127:88–93.
[16] Coppola A, Salatino P, Montagnaro F, Scala F. Hydration-induced reactivation of spent sorbents for fluidized bed calcium looping (double looping). Fuel Process Technol 2014;120:71–8.
[17] Antzara A, Heracleous E, Lemonidou AA. Improving the stability of synthetic CaO-basedCO_2 sorbents bystructural promoters. Applied Energy. 2015;156:331-43.
[18] Reddy GK, Quillin S, Smirniotis P. Influence of the synthesis method on the structure and CO_2 adsorption properties of Ca/Zr sorbents. Energy and Fuels 2014;28:3292–9.
[19] Ruff O, Ebert F, Stephan E. An article on highly fire resistant ceramic substances II The ZrO_2-CaO system. Zeitschrift fur Anorg und Allg Chemie 1929;180:215–24.
[20] Li C-C, Cheng J-Y, Liu W-H, Huang C-M, Hsu H-W, Lin H-P. Enhancement in cyclic stability of the CO_2 adsorption capacity of CaO-based sorbents by hydration for the calcium looping cycle. J Taiwan Inst Chem Eng 2014;45:227–32.